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(54) Title: BLENDS OF POLY(ETHYLENE THEREPHTHALATE) AND 4,4'-BIPHENYLDICARBOXYLIC ACID POL- YESTERS (57) Abstract Disclosed are blends of about 99 to about 10 weight % of poly(ethylene terephthalate) and about 1 to about 90 weight % of a polyester from 4,4'-biphenyldicarboxylic acid and at least one non-branched, aliphatic glycol having 2 to 6 carbon atoms. The blends have improved gas barrier and chemical resistance properties.		

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BLENDING OF POLY(ETHYLENE TEREPHTHALATE)
AND 4,4'-BIPHENYLDICARBOXYLIC ACID POLYESTERS

Field of Invention

5 The present invention is directed to blends of poly(ethylene terephthalate) and polyester from 4,4'-biphenyldicarboxylic acid and at least one aliphatic glycol. The blends have improved gas barrier and chemical resistance properties.

10

Background of the Invention

 Polyesters of 4,4'-biphenyldicarboxylic acid (BDA) and certain aliphatic glycols have been known in the art for decades. The homopolymers based on BDA are
15 described as very crystalline (see U.S. Patent 2,976,266, column 2, line 72, through column 3, line 1) and often are modified with other glycols to lower the polymer melting point. The glycols most often used are branched, aliphatic glycols such as
20 2,2-dimethyl-1,3-propanediol or polyether glycols such as polyethylene glycols or polytetramethylene glycols (U.S. Patent 3,261,812) or aliphatic-aromatic glycols such as p-xylene glycol (U.S. Patent 3,008,932). One
25 other method for lowering the melting point of the copolyesters is to reduce the biphenyldicarboxylic acid modifier content of the polymers by the addition of another aromatic dicarboxylic acid modifier such as terephthalic acid (U.S. Patent 4,082,731).

 Specifically, homopolyesters of
30 4,4'-biphenyldicarboxylic acid and certain aliphatic glycols are disclosed in journal literature. Homopolyesters of 4,4'-biphenyldicarboxylic acid and ethylene glycol, 1,4-butanediol, and 1,6-hexanediol are

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disclosed by Meurisse et al., in the British Polymer Journal, Volume 13, page 57 (1981) (Table 1). Jackson and Morris include a review of homopolyesters from 4,4'-biphenyldicarboxylic acid and various aliphatic glycols in the Journal of Applied Polymer Science, Applied Polymer Symposia, 41, 307-326 (1985). Krigbaum et al., disclose relatively low molecular weight homopolyesters from 4,4'-biphenyldicarboxylic acid and various aliphatic glycols in the Journal of Applied Polymer Science, Polymer Letters Edition, 20, 109-115 (1982). Low molecular weight homopolyesters of 4,4'-biphenyldicarboxylic acid are also disclosed by Wanatabe et al., Macromolecules, 21(1), p. 278-280 (1988), and Krigbaum et al., Polymer, 24(10), p. 1299-1307 (1983). Jpn. Kokai Tokkyo Koho JP 61,236,821 [86,236,821] (1986) also discloses low molecular weight polyesters from 4,4'-biphenyldicarboxylic acid and 1,4-butanediol prepared below their melting temperatures in a nonvolatile liquid. Polyesters of 1,6-hexanediol and 4,4'-biphenyldicarboxylic acid are disclosed in Kobunshi Ronbunshu, Vol. 44(12), 983-986 (December 1987) having limiting viscosity number of about 0.31.

U.S. 3,842,040 and U.S. 3,842,041 disclose the homopolyester of 4,4'-biphenyldicarboxylic acid and ethylene glycol.

Copolyesters of 4,4'-biphenyldicarboxylic acid (BDA) and certain aliphatic glycols are disclosed and ethylene glycol (EG), 1,4-butanediol (BD), 1,6-hexanediol (HD) are specifically disclosed in column 2, line 70 of U.S. 2,976,266 in a general listing along with other aliphatic glycols useful in this disclosed invention. However, copolyesters of BDA

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and linear, non-branched glycols are not specifically disclosed.

U.S. 4,742,151 discloses ultra-high-molecular weight polyesters prepared from aromatic dicarboxylic acids and alkylene glycols containing from 2 to 6 carbons having an intrinsic viscosity greater than 1.5. 4,4'-Biphenyldicarboxylic acid is disclosed in a list of dicarboxylic acids useful in the disclosed invention. Blends of these polymers with other polyesters are not disclosed.

German Offenlegungsschrift, DE 1935252, discloses polyesters of two aromatic dicarboxylic acids which include 10 to 50 mol % 4,4-biphenyldicarboxylic acid, 50 to 90 mol % of terephthalic acid and the two glycols ethylene glycol and 1,4-cyclohexanedimethanol.

Japanese patent, Kokai Tokkyo Koho JP 57/198726 discloses copolyesters containing 25 to 80 mol % 4,4'-biphenyldicarboxylic acid with various aliphatic glycols and aromatic dicarboxylic acids.

Heretofore, blends of PET and polyesters from 4,4'-biphenyldicarboxylic acid and at least one non-branched, aliphatic glycol having 2 to 6 carbon atoms have been unknown.

25 Summary of the Invention

The present invention is directed to a polymer blend comprising

(A) about 99 to about 10 weight % of poly(ethylene terephthalate) having an inherent viscosity of greater than or equal to about 0.4 determined at 25°C in 25/35/40 (wt./wt./wt.) phenol/tetrachloroethane/p-chlorophenol at a

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concentration of 0.1 gram (g)/100 milliliters (mL), and

- (B) about 1 to about 90 weight % of a polyester comprising repeating units of
- 5 4,4'-biphenyldicarboxylic acid and at least one non-branched, aliphatic glycol having 2 to 6 carbon atoms wherein said polyester has an inherent viscosity of greater than or equal to about 0.2 determined at 25°C in 25/35/40
- 10 (wt./wt./wt.) phenol/tetrachloroethane/p-chlorophenol at a concentration of 0.1 g/100 mL.

A preferred polymer blend of the present invention comprises a polymer blend comprising

- 15 (A) about 99 to about 10 weight % of poly(ethylene terephthalate) having an inherent viscosity of greater than or equal to about 0.4 determined at 25°C in 25/35/40 (wt./wt./wt.)
- 20 phenol/tetrachloroethane/p-chlorophenol at a concentration of 0.1 g/100 mL, and
- (B) about 1 to about 90 weight % of a homopolyester comprising of repeating units of
- 25 4,4'-biphenyldicarboxylic acid and diethylene glycol or 1,6-hexanediol, wherein said homopolyester has an inherent viscosity of greater than or equal to about 0.6 determined at 25°C in 25/35/40 (wt./wt./wt.)
- 30 phenol/tetrachloroethane/p-chlorophenol at a concentration of 0.1 g/100 mL.

Detailed Description of the Invention

The prior art discloses molding, spinning, and extrusion into film as viable processes for shaping the

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individual polyesters in the blend of this invention. Oriented or shaped objects from blends of poly(ethylene terephthalate) (PET) and BDA homopolyesters and copolyesters are not disclosed.

5 The blends of this invention provide a way of reducing the gas barrier properties of poly(ethylene terephthalate) which has begun to find wide commercial acceptance in food packaging and other miscellaneous applications. We have found, for example, that it is
10 very difficult or not even possible to biaxially orient on a T.M. Long film stretcher homopolyesters or copolyesters prepared from BDA and one or more aliphatic, non-branched glycols of the art. Generally, this is because the polymers are highly anisotropic
15 and/or highly crystalline. Film extruded from a die is often strong only in the direction of film extrusion. Anisotropy present in the extruded films can cause the films to crack or tear along the film extrusion direction as the film exits the die. The brittle
20 character of the extruded films can be caused by the highly crystalline nature of many of the BDA polyester films. It is usually not possible to prepare completely amorphous films by quenching films of many of the BDA homopolyesters of the art as is typical for
25 polyesters such as poly(ethylene terephthalate). Hence, when attempts are made to reheat extruded film of the neat BDA polyester prior to biaxial orientation, the films typically crystallize even more, preventing further extension of the polymer chains during biaxial
30 orientation. The films often tear when stretched 200% to 300% in a manner similar to PET and will not orient.

We have found that by blending these BDA polymers with PET, we are able to extrude tough films that are

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biaxially orientable. The presence of as little as 1 weight % of the BDA polyesters in PET acts to reduce the carbon dioxide transmission rate by about 15%.

Generally, raising the BDA polyester content to 50
5 weight % reduces the carbon dioxide transmission rate of PET about one half. The ability to biaxially orient the blends will allow one to use commercial stretch blow techniques for the manufacture of containers with superior gas barrier properties. For example, a 70/30
10 PET/(BDA)(DEG) blend (that is a blend of 30 weight % PET and 70 weight % of a (BDA)(DEG) homopolyester) would have about one half the carbon dioxide gas transmission rate of unmodified PET. One might be expected to prepare a carbonated beverage container from the blend
15 which would have about twice the shelf life of the unmodified stretch blow molded carbonated beverage container prepared from unmodified PET.

In the polymer blend of the present invention it is preferred that the weight % of component (A) is about 10
20 to 90, and the weight % of component (B) is about 90 to about 10.

It is also preferred that component (B) is a homopolyester of 4,4'-biphenyldicarboxylic acid and a glycol having 2 to 6 carbon atoms, or a copolyester of
25 4,4'-biphenyldicarboxylic acid and two glycols having 2 to 6 carbon atoms.

It is preferred that the aliphatic glycol of component (B) is 1,6-hexanediol, 1,4-butanediol, 1,3-propanediol, or 1,5-pentanediol.

30 The PET portion of the blends (i.e., component (A)) suitable for blending with the BDA polyester (i.e., component (B)) should have inherent viscosity (I.V.) of at least about 0.4, but preferably about 0.6 or more.

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The PET portion of the blend may also be modified with up to about 30 mol % of other glycols containing 2 to 16 carbon atoms or other aromatic acids having up to 16 carbon atoms. Examples of suitable dicarboxylic acid
5 modifiers include aliphatic dicarboxylic acids such as malonic, succinic, glutaric, adipic, pimelic, azelaic, suberic, sebacic, and dodecanedicarboxylic acids and aromatic dicarboxylic acids such as isophthalic acid,
10 4,4'-biphenyldicarboxylic acid, trans-4,4'-stilbene-dicarboxylic acid, 2,6-naphthalenedicarboxylic acid, 2-chloroterephthalic acid, and 2,5-dichloroterephthalic acid.

The glycol portion of the PET may be modified with various glycols which include 1,3-propanediol,
15 2,2-dimethyl-1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, p-xylenediol, and 1,3- or 1,4-cyclohexanedimethanol (trans and/or cis).

The BDA homopolyester and copolyester portion of the blends (i.e., component (B)) may be modified with up
20 to about 30 mol % of other aromatic dicarboxylic acids having up to 20 carbon atoms such as terephthalic acid, 2-chloroterephthalic acid, trans-4,4'-stilbenedicarboxylic acid, 2,6-naphthalene-dicarboxylic acid, and isophthalic acid so long as the
25 blends substantially retain their improved gas barrier properties. The BDA polyesters should have inherent viscosities of at least about 0.2, but preferably, at least about 0.6 or even about 1.0 or more.

It is preferred that component (B) is modified with
30 about 0 to about 20 mol % of said second modifier.

When the polymer blend of the present invention is in the form of an extruded film, it is preferred that

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said extruded film has a carbon dioxide permeability of less than or equal to 55 cc-mil/100 in²-24 hours-atm.

Other more specific polymer blends of the present invention include:

- 5 (1) wherein the glycol component of component (B) comprises about 30 to 95 mol % 1,6-hexanediol, and about 5 to 70 mol % ethylene glycol, and
- (2) wherein the glycol component of component (B) comprises about 5 to 95 mol % 1,4-butanediol and 5 to 95 mol % 1,6-hexanediol.

10 The following examples are to illustrate the invention but should not be interpreted as a limitation thereon.

15 The inherent viscosities of the polyesters are determined in 25/35/40 phenol/tetrachloro-ethane/p-chlorophenol at 25°C at concentration of 0.1 g/100 mL. The polyesters are ground, dry-blended, dried at 100°C, and extruded and pelletized on a Werner-Pfleiderer extruder or on a 3/4-in. Brabender
20 extruder at 240° to 300°C. The blends are redried at 100°C and extruded into film that is 20-mil thick and about 6 inches (in.) wide. The films are biaxially oriented on a T.M. Long film stretcher and submitted for gas permeability testing. The oxygen permeability is
25 determined on a Mocon Model 1000 or Model 10/50 oxygen permeability tester at 30°C and 68% relative humidity and the carbon dioxide permeability is determined on a Mocon PermTRAN C IV permeability tester at 0% relative humidity.

30 EXAMPLE 1

This example illustrates the preparation of the homopolyester consisting of 100 mol % 4,4'-biphenyl-

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dicarboxylic acid units and 100 mol % 1,6-hexanediol units.

A mixture of 162.0 g (0.60 mol) dimethyl 4,4'-biphenyldicarboxylate, 85.0 g (0.72 mol) 1,6-hexanediol, and 0.14 g titanium tetraisopropoxide is placed in a 1-L flask equipped with an inlet for nitrogen, a metal stirrer, and a short distillation column. The flask is heated at 240°C for about 1 hour, at 260°C for about 1/2 hour, and a vacuum of 0.5 millimeters (mm) is gradually applied over the next 5 minutes. Full vacuum is maintained for about 1 hour. A high melt viscosity, white crystalline polymer is obtained with an I.V. of 1.30 and a melting endotherm measured by Differential Scanning Calorimetry (DSC) at 217°C.

EXAMPLE 2

A polyester is prepared to an I.V. of 1.25 similar to that of Example 1, ground, and solid-state polymerized by heating 1 hour at 110°C and then for 4 hours at 210°C to give a polymer with an I.V. of 2.26.

EXAMPLE 3

This example illustrates the extrusion and film stretching of PET 7352 (I.V. = 0.85) obtained from Eastman Chemicals Products, Inc.

PET 7352 is extruded into film at 280°C and stretched 4X by 4X or 300% on the T.M. Long film stretcher. The biaxially oriented film has an oxygen permeability of 6.1 cc-mil/100 in²-24 hr-atm and a carbon dioxide permeability of 31.5 cc-mil/100 in²-24 hr-atm.

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EXAMPLE 4

This example illustrates the extrusion and film stretching of a 70/30 wt./wt. blend of PET 7352 and (BDA) (DEG) polyester. A polymer of BDA and diethylene glycol is prepared according to the procedure of Example 1, ground to pass a 3-mm screen, and dry blended with 70 weight % PET 7352 (I.V. = 0.85, Eastman Chemicals Products, Inc.). The blend is extruded and pelletized, and then extruded into film, and subsequently biaxially oriented 3X by 3X or 200% on a T.M. Long film stretcher at 100°C. The oriented film has an oxygen permeability of 3.2 cc-mil/100 in² 24 hr-atm and a carbon dioxide permeability of 16.2 cc-mil/100 in² 24 hr-atm.

The other polyesters and blends shown in Tables 1 and 2 are prepared according to procedures similar to those described in Examples 1 and 2 above.

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Table 1

Gas Barrier Properties of Films of
PET/(BDA)(HD) Polyester/Polyester Blends

	PET 7352 Content, wt. %	(BDA)(HD) Content, wt. %	Gas Permeability, cc-mil/24 hr-atm			
			PO2 Ext.	Oriented	PCO2 Ext.	Oriented
10	100 (control) ^a	0	12.4	6.1	65.3	31.4
	99 ^a	1	13.7	6.1	-	36.5
	95 ^a	5	13.2	7.9	54.8	30.3
	90 ^a	10	12.3	6.6	50.6	29.7
15	80 ^a	20	10.7	5.8	57.3	-
	70 ^b	30	8.1	5.1	37.3	24.8
	50 ^c	50	6.9	-	-	-

20 ^a These films were biaxially oriented 300% on a T.M. Long Film Stretcher at 100°C.

^b These films were biaxially oriented 200% on a T.M. Long Film Stretcher at 100°C.

25 ^c This film could not be biaxially oriented at 100°C and was too brittle.

30 Codes: PO2 = oxygen permeability,
PCO2 = carbon dioxide permeability,
BDA = 4,4'-biphenyldicarboxylic acid, and
HD = 1,6-hexanediol.

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Table 2

Gas Barrier Properties of Films of
PET/(BDA)(DEG) Polyester/Polyester Blends

	PET 7352 Content, wt. %	(BDA)(DEG) Content, wt. %	Gas Permeability, cc-mil/100 in ² 24 hr-atm			
			PO ₂		PCO ₂	
			Ext.	Oriented	Ext.	Oriented
10	100 (control) ^a	0	12.4	6.1	65.3	31.4
	99 ^a	1	10.8	7.2	41.9, 54.6	30.8
15	95 ^a	5	10.8	5.8	52.0	28.8
	90 ^a	10	10.0	4.9	45.7	29.5
	80 ^a	20	8.7	3.7	42.0	22.8
	70 ^b	30	6.9	3.2	27.7	16.2
	70 ^{a,c}	30	7.3	3.2	28.6	18.4
20	50 ^b	50	4.0	2.3	11.6	16.5
	30 ^d	70	-	-	-	-

^a These films were biaxially oriented 300% on a T.M.
Long Film Stretcher at 100°C.

^b These films were biaxially oriented 200% on a T.M.
Long Film Stretcher at 100°C.

^c The PET used in this blend is PET 10388 (I.V. = 1.12)
obtained from Eastman Chemicals Products, Inc.
Kingsport, Tennessee.

^d This film could not be biaxially oriented at 100°C.

Codes: PO₂ = oxygen permeability,
PCO₂ = carbon dioxide permeability,
BDA = 4,4'-biphenyldicarboxylic acid, and
DEG = diethylene glycol.

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The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and
5 scope of the invention.

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CLAIMS

1. A polymer blend comprising

5 (A) about 99 to about 10 weight % of
poly(ethylene terephthalate) having an
inherent viscosity of greater than or
equal to about 0.4 determined at 25°C in
25/35/40 (wt./wt./wt.)

10 phenol/tetrachloro-ethane/p-chlorophenol
at a concentration of 0.1 g/100 mL, and

(B) about 1 to about 90 weight % of a
polyester comprising repeating units of
15 4,4'-biphenyldicarboxylic acid and at
least one non-branched, aliphatic glycol
having 2 to 6 carbon atoms wherein said
polyester has an inherent viscosity of
greater than or equal to about 0.2
20 determined at 25°C in 25/35/40
(wt./wt./wt.) phenol/tetrachloro-
ethane/p-chlorophenol at a concentration
of 0.1 g/100 mL.

25 2. The polymer blend of Claim 1 wherein
component (B) is a homopolyester of
4,4'-biphenyldicarboxylic acid and a glycol having 2 to
6 carbon atoms, or a copolyester of
4,4'-biphenyldicarboxylic acid and two glycols having 2
30 to 6 carbon atoms.

3. The polymer blend of Claim 1 wherein the

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weight % of component (A) is about 10 to about 90 and the weight % of component (B) is about 90 to about 10.

4. The polymer blend of Claim 1 wherein said
5 aliphatic glycol of component (B) is 1,6-hexanediol, 1,4-butanediol, 1,3-propanediol, or 1,5-pentanediol.

5. The polymer blend of Claim 2 wherein the
weight % of component (A) is about 80 to about 20 and
10 the weight % of component (B) is about 20 to about 80.

6. The polymer blend of Claim 2 wherein the
glycol component of component (B) is 1,6-hexanediol,
1,4-butanediol, 1,3-propanediol, or 1,5-pentanediol.
15

7. The polymer blend of Claim 1 wherein said
poly(ethylene terephthalate) of component (A) is
modified to contain 0 to about 30 mol % of at least one
first modifier which is a glycol having 2 to 16 carbon
20 atoms, a dicarboxylic acid having up to 16 carbon atoms,
or a mixture thereof, and wherein said polyester of
component (B) is modified to contain 0 to about 30 mol %
of a second modifier which is a different aromatic
dicarboxylic acid having up to 16 carbon atoms or a
25 mixture of said different aromatic dicarboxylic acids,
provided that at least one of component (A) or component
(B) is modified with greater than 0 mol % of an
appropriate modifier.

30 8. The polymer blend of Claim 7 wherein said
poly(ethylene terephthalate) of component (A) is
modified with about 0 to about 20 mol % of said first
modifier.

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9. The polymer blend of Claim 7 wherein said polyester of component (B) is modified with about 0 to about 20 mol % of said second modifier.

5

10. The polymer blend of Claim 7 wherein said dicarboxylic acid of said first modifier is malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, azelaic acid, suberic acid, sebacic acid, dodecanedicarboxylic acid, trans-4,4'-stilbenedicarboxylic acid, 2,6-naphthalenedicarboxylic acid, isophthalic acid, 2-chloroterephthalic acid, or 2,5-dichloroterephthalic acid; said glycol of said first modifier is 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, or 1,6-hexanediol, and said second modifier of component (B) is terephthalic acid, 2-chloroterephthalic acid, trans-4,4'-stilbenedicarboxylic acid, 2,6-naphthalenedicarboxylic acid, or isophthalic acid.

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11. The polymer blend of Claim 1 wherein the inherent viscosity of component (A) is greater than or equal to about 0.6, and the inherent viscosity of component (B) is greater than or equal to about 0.6.

25

12. The polymer blend of Claim 1 in the form of an extruded film having a carbon dioxide permeability of less than or equal to 55 cc-mil/100 in²-24 hours-atm.

30

13. The polymer blend of Claim 1 wherein the glycol component of component (B) comprises about 30 to 95 mol % 1,6-hexanediol, and about 5 to 70 mol % ethylene glycol.

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14. The polymer blend of Claim 1 wherein the glycol component of component (B) comprises about 5 to 95 mol % 1,4-butanediol and 5 to 95 mol % 1,6-hexanediol.

15. The polymer blend of Claim 1 wherein said blend is capable of being biaxially oriented.

16. A polymer blend comprising

(A) about 99 to about 10 weight % of poly(ethylene terephthalate) having an inherent viscosity of greater than or equal to about 0.4 determined at 25°C in 25/35/40 (wt./wt./wt.) phenol/tetrachloro-ethane/p-chlorophenol at a concentration of 0.1 g/100 mL, and

(B) about 1 to about 90 weight % of a homopolyester comprising of repeating units of 4,4'-biphenyldicarboxylic acid, and diethylene glycol or 1,6-hexanediol, wherein said homopolyester has an inherent viscosity of greater than or equal to about 0.6 determined at 25° C in 25/35/40 (wt./wt./wt.) phenol/tetrachloro-ethane/p-chlorophenol at a concentration of 0.1 g/100 mL.

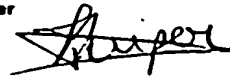
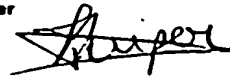
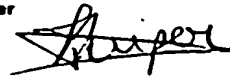
17. The polymer blend of Claim 16 wherein the polyester of component (B) is modified to contain greater than 0 and up to about 30 mol % of at least one

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of terephthalic acid, 2-chloroterephthalic acid,
isophthalic acid, or 2,6-naphthalenedicarboxylic acid.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 89/05725

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁵ : C 08 L 67/02, //(C 08 L 67/02, 67:02)											
II. FIELDS SEARCHED Minimum Documentation Searched ⁷ Classification System Classification Symbols IPC ⁵ C 08 L Documentation Searched other than Minimum Documentation to the Extent that such Documents are included in the Fields Searched ⁸											
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹ <table border="1"> <thead> <tr> <th>Category ¹⁰</th> <th>Citation of Document, ¹¹ with Indication, where appropriate, of the relevant passages ¹²</th> <th>Relevant to Claim No. ¹³</th> </tr> </thead> <tbody> <tr> <td>X</td> <td>Chemical Abstracts, volume 80, no. 8, 25 February 1974, (Columbus, Ohio, US) see page 33, abstract 37881r, & JP, A, 7340847 (TEIJIN LTD.) 15 June 1973</td> <td>1-9,15</td> </tr> <tr> <td>X</td> <td>Chemical Abstracts, volume 82, no. 4, 27 January 1975, (Columbus, Ohio, US) see page 54, abstract 17814j, & JP, A, 7476947 (TEIJIN LTD.) 24 July 1974</td> <td>1-9,15</td> </tr> </tbody> </table>			Category ¹⁰	Citation of Document, ¹¹ with Indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	X	Chemical Abstracts, volume 80, no. 8, 25 February 1974, (Columbus, Ohio, US) see page 33, abstract 37881r, & JP, A, 7340847 (TEIJIN LTD.) 15 June 1973	1-9,15	X	Chemical Abstracts, volume 82, no. 4, 27 January 1975, (Columbus, Ohio, US) see page 54, abstract 17814j, & JP, A, 7476947 (TEIJIN LTD.) 24 July 1974	1-9,15
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<p>¹⁰ Special categories of cited documents: 10</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"A" document member of the same patent family</p>											
IV. CERTIFICATION <table border="1"> <tr> <td>Date of the Actual Completion of the International Search 30th March 1990</td> <td>Date of Mailing of this International Search Report 03.05.90</td> </tr> <tr> <td>International Searching Authority EUROPEAN PATENT OFFICE</td> <td>Signature of Authorized Officer Mme N. KUIPER </td> </tr> </table>			Date of the Actual Completion of the International Search 30th March 1990	Date of Mailing of this International Search Report 03.05.90	International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer Mme N. KUIPER 					
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